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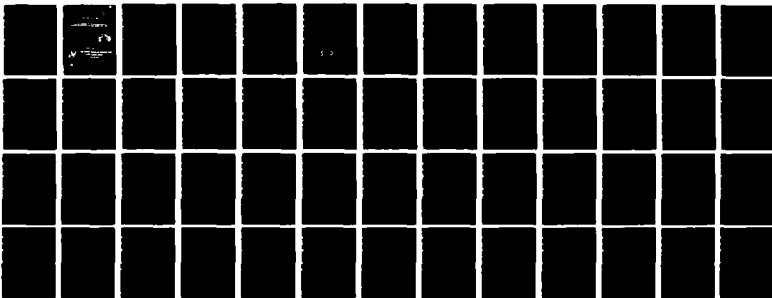
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RESEARCH AND DEVELOPMENT CENTER DOVER NJ ARMAHE
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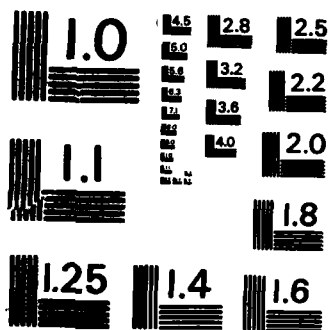
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) CARS spectra were obtained for a $\phi = 3.2$ CH ₄ /N ₂ O model and nitramine propellant flames throughout the reaction and post-flame zones in order to assess kinetic mechanisms occurring in these flames. Spectra were obtained in the regions of 4200 - 3900, 2400 - 2050, and 1900 - 1200 cm ⁻¹ . The reaction zone of the rich CH ₄ /N ₂ O flame was studied primarily to provide a stationary flame analog to the transient propellant flame. In the CH ₄ /N ₂ O flame, the decay of the initial products was observed through the Q-branch of the ν_1 and ν_3 modes (cont)		

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20. ABSTRACT (cont)

of N₂O and the Q, O, and S branches of the ν_2 and $2\nu_2$ modes of CH₄. The formation of the products N₂, H₂ [$Q(\nu'' = 0$ and $\nu'' = 1)$ and S(5) - S(9)], CO, and CO₂ (ν_1) were also observed. Temperatures were obtained from both the H₂ and N₂ Q-branches. In the nitramine propellant flame, the upper bound of the gas-surface interface temperature was measured as $900 \text{ K} \pm 100 \text{ K}$ from the H₂ Q-branch. Near the surface of the propellant, reactant RDX (1599 cm^{-1} tentatively assigned as asymmetric NO₂ stretch) and transients HCN (ν_1) and NO are observed at moderate concentration ($>1\%$). The final product N₂ is observed at low concentration ($\sim 1\%$), H₂ (Q and S branches) and CO are observed at higher concentration ($>10\%$). RDX and HCN decay within 2 mm of the propellant surface while NO remains constant until 4 mm where it decays with a concomitant rise in N₂ concentration and temperature. H₂ and CO also increase in temperature and concentration.

The reaction zone of nitramine propellant is seen to consist of two characteristic areas: (1) an inner flame area near the solid gas-interface which is at a temperature of $900 \pm 100 \text{ K}$ and is characterized by the gas-phase reactions of RDX and HCN that provide the heat that determines the burning rate, and (2) an outer flame area farther upstream where NO is converted to N₂ to generate the luminous flame.

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INTRODUCTION

Obtaining direct experimental information on the dynamics of the deflagration and detonation of energetic materials has been difficult with the use of conventional optical techniques. The advent of nonlinear optical techniques such as Coherent Anti-Stokes Raman Scattering (CARS) provides an opportunity to extend the information obtainable on energetic systems. Propellant flames are often transient, particle-laden, incandescent, and, under some conditions, turbulent. However, single-shot CARS spectra were obtained from the post-flame region of double-base propellant flames (Harris and McIlwain, refs 1 and 2). This demonstration of the direct applicability of CARS to obtaining temperature and concentration from propellant flames led to further investigations in the reaction zone and post-flame region of $\text{CH}_4/\text{N}_2\text{O}$ model propellant flames (Harris, refs 3 and 4 and Aron et al., ref 5). These studies were then extended to the reaction zone of nitramine propellant flames through measurements at the surface and at 6-mm above the propellant surface (Aron and Harris, ref 6 and Harris, ref 7). In these studies both the spectral and spatial ranges are extended for the reaction zone of $\text{CH}_4/\text{N}_2\text{O}$ and nitramine propellant flames. Rich $\text{CH}_4/\text{N}_2\text{O}$ flames are used as stationary model flames of the transient propellant flames.

The combustion of nitramine propellants was reviewed recently by Boggs (ref 8) and Schroeder (ref 9). Nitramine propellants contain a substantial percentage of nitramines (~76%) along with a small percentage of energetic binder (~4% nitrocellulose) and/or organic-ester binders. Current models of nitramine propellant combustion are essentially models of HMX (cyclotetramethylene tetranitramine) and RDX (hexahydro-1,3,5-trinitro-s-triazine deflagration). The burning rate expression for nitramine propellants (Ben-Reuven and Caveny, ref 10)

$$r = ap^{1/2} (1 + p/b)^{1/2}$$

is such that at low pressure

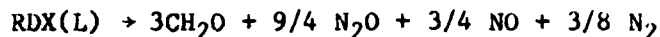
$$p \ll b, r \sim p^{1/2}$$

whereas at high pressure

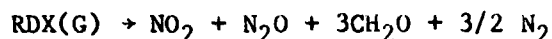
$$p \gg b, r \sim p^1$$

Much of the modeling of nitramine propellant has been to explain this complex burning rate behavior. Ben-Reuven and Summerfield (ref 11) have reviewed nitramine propellant modeling and derived improvements to the comprehensive model of nitramine deflagration (Ben-Reuven and Caveny, ref 10). The Ben-Reuven and Caveny model consists of the following mechanism:

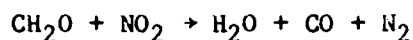
First, partial decomposition of RDX in the liquid phase



Next, gas phase decomposition of RDX in the near field (close to the propellant surface)



Finally, oxidation of formaldehyde by NO_2



in the far field (relatively far from the propellant surface).

Thermocouple measurements of temperature profiles in nitramine/polyurethane composite propellants were made by Kubota (ref 12). He obtained surface temperatures between 690 K to 730 K in the pressure range between 10 to 30 atm. Kubota found from flame quenching studies that both RDX and the polymeric binder melt at the surface to produce an homogeneous liquid layer that produces an homogeneous flame. The flame was found to consist of dark and luminous flame zones with the luminous zone approaching the propellant surface with increasing pressure. The measured dark zone thickness at 20 atm for a 75% RDX formulation was 2-mm. The dark zone thickness was observed to vary inversely with the square of increasing pressure. At 1,000 psi, the dark zone would be compressed to 200 μm , spatially limiting accessibility for optical diagnostics. The luminous flame, however, would still be accessible to optical diagnostics. According to Kubota, the dark zone reaction can be attributed to NO reduction to N_2 to produce the luminous flame. The burning rate was found to be controlled not by the luminous flame but rather by exothermic reactions of RDX at the propellant surface.

Ben-Reuven and Summerfield (ref 11) have added to the Ben-Reuven and Caveny (ref 10) model, a nonequilibrium evaporation law at the melt-gas interface, an improved melt phase model including a decomposition-gas bubble, and an improved model for far-field processes including several simultaneous secondary reactions.

Schroeder (ref 9) has reviewed nitramine decomposition chemistry. At low temperature (500 to 600 K), the gas phase reaction mechanism by which RDX initially decomposes is postulated as



This is thought to occur through HONO elimination and/or cyclic decomposition via the intermediate N-nitroformimine, CH_2NNO_2 . Crossover to a high temperature reaction mechanism in the gas phase is thought to occur above about 600 K.

This mechanism is thought to occur via breakage of an initial NN bond followed by fragmentation to CH_2NNO_2 which decomposes to HCN and NO_2 , leading to the overall initial reaction.



The liquid phase reaction is also thought to occur by a mechanism similar to the high temperature gas phase reaction mechanism.

Price et al. (ref 13) modified the Beckstead-Derr-Price (BDP) framework for HMX decomposition to incorporate both the high (endothermic) and low (exothermic) temperature nitramine decomposition mechanisms in the solid and exothermic and endothermic second-order reactions in the gas phase. Cohen et al. (ref 14) explicitly included reactions of HCN and NO in the BDP model.

Miller and Coffee (refs 15 and 16) gave detailed comparisons of the various methods used to model propellant combustion. Their assessment was that the methods place too much emphasis on matching experimental burning rate data which are relatively insensitive to mechanistic details. They conclude that mechanisms used in propellant modeling should be independently validated. Propellant surface temperature, T_s , enters many of these models as a parameter used to match experimental burning rates. Independent measurement of T_s will allow validation and further development of these models.

CARS spectroscopy, which was reviewed by Druet and Taran (ref 17) and Ecbreth and Schreiber (ref 18), provides an ideal tool for the further elucidation of nitramine propellant kinetic mechanisms. CARS has the necessary spatial (100 μm), temporal (10 ns single shot), and spectral resolution to provide the detailed temperature, concentration, and rovibrational state distribution profiles necessary to successfully model propellant flames from independently measured elementary kinetic reactions (Gardner, ref 19).

EXPERIMENTAL

CARS spectra are generated with folded BOXCARS to achieve phase matching. The output of a Quanta-Ray DCR-2A Nd/YAG laser at 1.06 μm (700 mj) is doubled to generate the pump beam at 5320A (250 mj) with a bandwidth of near 1 cm^{-1} . The pump beam is separated from the primary beam with prisms. The pump beam is split to generate ω_{1s} and ω_{1p} . ω_{1s} is used to pump a dye laser to generate the Stokes beam, ω_2 . The dye laser consists of a flowing dye cell in a planar Fabry-Perot oscillator cavity pumped slightly off axis by 20% of ω_{1s} with the output amplified by an additional flowing dye cell pumped by the remainder of ω_{1s} . The dye laser is operated broadband with the laser dyes given in table 1. To achieve BOXCARS geometry, ω_{1p} is reflected onto the front surface of a dichroic mounted at a 45 degree angle. The dichroic reflects 50% of ω_{1p} from half of its front surface and 100% of the remainder of ω_{1p} from its back surface while transmitting ω_2 which is introduced from the rear below ω_{1p} . ω_{1p} is split into two beams, ω_1

and ω_1' , such that at the focusing lens (200 mm focal length) ω_1 , ω_1' , and ω_2 are parallel and situated on a circle of 12.5 mm diameter with ω_1 and ω_1' on the central horizontal plane of the lens with ω_2 in the central vertical plane. Telescopes are inserted in the ω_1 and ω_2 beams to allow the focal spots to be equalized and intersecting. This was achieved with 0.85 and 2 X Galilean telescopes in ω_1 and ω_2 , respectively. A 5-mm-diameter iris centered on ω_1 prior to splitting further restricts intersection to the central portion of ω_1 . To optimize phase matching, a 12.5-mm-thick optical flat--rotatable about its horizontal axis--is inserted into ω_2 before the focusing lens. After passage through the sample, the beams are recollimated with a 200-mm focal length lens, after which ω_3 is located below the plane of ω_1 and ω_1' . ω_1 , ω_1' , and ω_2 are terminated with a neutral density filter. ω_3 is then focused with a 100-mm focal length lens onto the slits of a 1/3-m monochromator equipped with a 2,400 line/mm holographic grating and 100 μ m slits. The signal is detected by a PAR SIT detector and processed by a PAR OMA2 system. The full width at half-height (FWHH) of calibration lines near the center of the SIT detector is near 3.0 cm^{-1} , giving approximately 1 cm^{-1} per channel over the spectral range investigated.

Stationary flame measurements were made on a premixed $\text{CH}_4/\text{N}_2\text{O}$ flame maintained on a circular burner with a 2.0-cm-diameter head. The burner surface was constructed of a matrix of steel syringe needles of 0.09-cm outer diameter, so that a flat flame would be achievable under suitable flow conditions. Matheson technical grade methane and chemically pure nitrous oxide were separately flowed through 603 Matheson rotameters prior to premixing. The flow through the burner was adjusted to 13 cm/sec to maintain a 3.2 equivalence ratio (ϕ) flame where ϕ is defined here as the fuel/oxidant ratio divided by the stoichiometric fuel/oxidant ratio. At this flow, there is a dark zone extending about 5-mm above the burner surface followed by a dark yellow reaction zone extending to about 13-mm above the burner. A bright yellow post flame region surrounded by a light blue afterburning diffusion flame was situated above the reaction zone. To obtain CARS spectra in the reaction zone, the center of the burner surface was displaced vertically with a translation stage from the focus of ω_1 , ω_1' , and ω_2 to 2 cm below the focus. Spectra were obtained at intervals of 0.5 mm (0.25 mm in the vicinity of the reaction zone). The flame exhibited macroscopic structure since the position of the reaction zone fluctuated with respect to the burner surface. Spectral scans through the reaction zone were obtained in periods of stability between these large scale fluctuations. Spectra obtained at the same positions relative to the position of initial attainment of full flame temperature were reproducible within the precision of the flowmeters.

The nitramine propellant grains were 14 x 14 mm cylinders of mass 3.2 g. The propellant grains were burned in air with spectra taken along the centerline above the burning propellant surface during the approximately 1-minute burn time. The propellant flame can be characterized as consisting of an inner dark zone approximately 4 mm thick, a bright yellow post flame region, and an outer blue diffusion flame. The calculated gas velocity from the burning cylinder is approximately 50 cm/sec.

RESULTS

Theory

The observed CARS spectrum is proportional to the square of the modulus of the third-order susceptibility, $\chi^{(3)}$, which is the sum of a resonant term χ_r related to a nuclear displacement and χ_{nr} related to electronic displacement:

$$\chi^{(3)} = \chi_r + \chi_{nr} \quad (1)$$

The resonant term can be considered as a sum of Lorentzian line shapes of each Q(J), O(J), or S(J) transition (Tolles et al., ref 20 and Hall, ref 21).

$$\chi_r = \sum_j \frac{k_j \Gamma_j}{2\Delta\omega_j - i \Gamma_j} \quad (2)$$

where

$$k_j = (N/m\omega_0) |M_j|^2 (\Delta j) \Gamma_j^{-1} \quad (3)$$

where M_j , Δj , Γ_j are the polarizability matrix element, normalized population difference, and line width, respectively; $\Delta\omega_j$ is $\omega_2 - \omega_1 - \omega_j$; m is the reduced mass; and ω_0 is the resonant Raman frequency. $M = \alpha^2 (\nu + 1)^j$ and $7/45 b_j \pm 2^j \gamma^2 (\nu + 1)$ for Q and O, S branches, respectively. Where α , γ , and b_j are the derivatives of the mean isotropic and anisotropic molecular polarizability, and b_j are the Placzek-Teller coefficients, ν is the vibrational quantum number and $(\nu + 1)$ is contributed by the vibrational matrix element. The observed spectrum is convoluted over the laser linewidths and instrumental slit function.

χ_r is the sum of real and imaginary components χ' and χ'' , respectively, such that

$$|\chi^{(3)}|^2 = \chi'^2 + 2\chi'\chi'' + \chi''^2 + \chi_{nr}^2 \quad (4)$$

χ' and χ'' display dispersive and resonant behavior, respectively. Normalizing equation 4 with respect to the observed χ_{nr}^2 at the resonance gives

$$\left(\frac{|\chi^{(3)}|^2}{\chi_{nr}^2} \right)_0 = \left| \frac{\chi' + i\chi''}{\chi_{nr}} + 1 \right|^2 \quad (5)$$

where $\bar{\chi}$ and \bar{k} are defined as χ/N and k/N , respectively and $X_i = N/N_T$ with N and N_T , the number density of the resonant species and the total number density, respectively.

Summing of equation 5 over the populated levels gives:

$$\Sigma I_{\text{corr}}^2 = \Sigma (1/g_j)^2 (|\chi^{(3)}|^2 / \bar{\chi}_{\text{nr}}^2)_{\text{o}} = \left[X_i \frac{\Sigma \bar{k}_j}{\bar{\chi}_{\text{nr}}} + 1 \right]^2 \quad (6)$$

where $\bar{k}_j = \frac{1M_l^2}{m \omega_o \Gamma_j}$ since $\Sigma \Delta_j / g_j = 1$

$g_j = (\nu + 1)$ for Q branches without rotational structure and $(2J + 1) n_j (\nu + 1)$ for O and S branches where n_j is the nuclear spin degeneracy. Γ_j is taken as the experimentally observed spectral line width, Γ_{exp} , since the observed CARS intensity, $|\chi^{(3)}|^2$, is convoluted by the instrument function. If the peak height is measured from the maximum to the minimum of the resonant peak modulation of the nonresonant background spectra, only the imaginary term is measured (Tolles et al., ref 20) so that

$$X_i = \frac{(\Sigma I_{\text{corr}})^{1/2}}{(\Gamma_{\text{exp}} m \omega_o) \bar{\chi}_{\text{nr}} / \bar{M}^2} \quad (7)$$

with $\bar{M} = \alpha^2$ and $7/45 \gamma^2$ for Q branches (where anisotropic contributions are neglected) and O,S branches, respectively. Equation 7 forms the basis for a qualitative interpretation of the spectra. Concentration and temperature are separable such that concentration is related to the sum of I_{corr} while temperature is related to the ratio of I_{corr} of populated levels. Equation 7 was used to obtain relative concentrations through the reaction zone discussed below. In addition, for N_2 and H_2 the spectra were synthesized using the method of Hall (ref 21) and fitted to the experimental spectra using a least-square procedure to obtain temperature and concentration.

CH₄/N₂O Flames

Thermochemical calculations (Gordon and McBride, ref 22) were performed for $\phi = 3.2$ CH₄/N₂O. The calculated flame temperature was 1745 K with 23% CO, 1% CO₂, 42% H₂, 5% H₂O, and 29% N₂. CARS spectra were obtained in the regions 4200 to 3900, 2400 to 2050, and 1900 to 1200 cm⁻¹ as a function of distance above the center of the surface of the burner. The spectra are given in figures 1 through 7 and summarized in table 2.

Reaction occurs over a region extending from 2 mm to 12 mm with the steepest concentration gradients occurring between 6 mm to 10 mm. The flame may be roughly characterized as consisting of a dark or preheating zone extending from the surface to 6 mm, a reaction zone extending from 6 mm to 10 mm and a post flame region above 10 mm. The spectra shown in figures 1 through 6 show one representative spectra from each of these regions.

The spectra shown in figure 1 show the decay of reactant N_2O and the increase of the products N_2 , CO , and H_2 . The N_2O ν_3 at 2222 cm^{-1} and associated hot bands already have been observed and assigned from spectra occurring in the reaction zone of lean CH_4/N_2O flames (Harris, refs 23 and 24). The N_2 and CO vibrational and the H_2 pure rotational S(7) [The notation used is S(ν'')] spectra have previously been discussed for spectra arising from the post flame region of rich CH_4/N_2O flames (Aron et al., ref 5). The simultaneous observation of the decay of N_2O and the increase of the three principal products provides an opportunity to obtain concentration gradients to test kinetic mechanisms.

Spectra shown in figure 2 show the decay of the other reactant together with the increase of product H_2 S(7) and S(6) pure rotational lines. The CH_4 structure shown in figure 2 is assigned to ν_2 transitions. The prominent features of the methane transitions are observed* at the following frequencies (cm^{-1}): 1531, 1562, 1583, 1606, 1628, 1653, 1676, 1722, 1745, 1769, and 1792. This is in agreement with previously observed (Champion and Berger, ref 25) and calculated (Gray and Robiette, ref 26) Raman lines at the following frequencies (cm^{-1}): 1534 (Q), 1566 [S(0)], 1587 [S(1)], 1610 [S(2)], 1632 [S(3)], 1654 [S(4)], 1677 [S(5)], 1724 [S(7)], 1746 [S(9)], and 1770 [S(10)], assuming a separation of 4B for a ground state B value of 5.24 cm^{-1} (Gray and Robiette, ref 26).

N_2O and H_2 S(5) spectra are shown in figure 3. The N_2O CARS at 1284, 1290, and 1295 cm^{-1} transitions (not previously reported) are assigned to the ν_1 and $\nu_1 + \nu_2 - \nu_2$ and $\nu_1 + 2\nu_2 - 2\nu_2$ in agreement with transitions observed¹ in the Raman at 1285 cm^{-1} and calculated at 1289.7 cm^{-1} (Herzberg, ref 27). The ν_1 transition has a larger Raman cross section than the ν_3 together with hot bands populated at low temperature, providing an attractive option for quantitative temperature and concentration profiles in the reaction zone.

The decay of the CH_4 2 ν_2 band is shown in figure 4. The observed bands (cm^{-1}) are 3101 (Q), 3129 [S(0)], 3149 [S(1)], 3168 [S(2)], 3182 [S(3)], 3205 [S(4)], 3223 [S(5)], 3235 [S(6)], and 3258 [S(7)]. These are in agreement with assignments given by Hunt et al. (ref 28). Hydrogen Q band structure as it increases through the reaction zone is given in figure 5. Hydrogen is seen at a concentration less than 1% at 4 mm. The line positions as shown for $\nu'' = 0$ in figure 5 and $\nu'' = 0\text{ J} < 11$ and $\nu'' = 1\text{ J} < 9$ in figure 6 and the S bands $J = 5$ to 9 have been shown to be in excellent agreement with the results of constants derived from ab initio calculations (Fendell et al., ref 29) and constants (Dabrowski, et al., ref 30) derived from the $B^1\Sigma^+ \leftarrow X^1\Sigma^+$ and $C^1\Pi \leftarrow X^1\Sigma^+$ band of H_2 (Haw et al., ref 31).

Temperature was calculated from the $\nu'' = 0$ Q branch throughout the reaction zone. From 4 to 8 mm, there is a gradual increase in temperature from 500 K to 900 K and the distribution appears Boltzmann. Above 8 mm, there is an apparent bimodal distribution in which approximately half of the observed spectra have Boltzmann distributions consistent with the random experimental error while the other spectra show much larger deviations from the Boltzmann distribution (greater than 2 σ) than the random experimental error. In these non-Boltzmann distributions, the odd levels are preferentially populated over the even levels with

* Some lines were observed with the use of other dyes.

the higher J value of both even and odd levels showing excess population. At present, it is not certain whether these apparently non-Boltzmann distributions reflect the actual hydrogen rotational distributions, instrument errors, or flame instability for hydrogen above the reaction zone. Flame stability lessens with distance above the burner. The outer blue diffusion flame is noticeably floppy. Further work is being done in more stable rich $\text{CH}_4/\text{N}_2\text{O}$ flames to clarify the interpretation of the hydrogen Q branch spectra. The H_2 spectra that have Boltzmann distributions give results consistent with temperatures obtained from N_2 CARS spectra and thermochemical calculations.

N_2 CARS spectra in the reaction zone are difficult to interpret because of the unknown non-resonant susceptibility. However, in the post flame region least-squares-fits to the N_2 spectra give a temperature of 1890 ± 100 K and concentration of 0.26 ± 0.05 m (mole fraction) which are close--although slightly high for temperature--to the results of the thermochemical calculations.

Nitramine Propellant Flames

Thermochemical calculations (Gordon and McBride, ref 22) were performed for the nitramine propellant with the result that the adiabatic, constant pressure, flame temperature was calculated as 2076 K with the equilibrium final products calculated as 38% CO , 27% H_2 , 22% N_2 , 10% H_2O , and 3% CO_2 . CARS spectra were obtained in the regions 4200 to 3900, 2400 to 2050, and 1900 to 1200 cm^{-1} both as a function of distance above the center of the propellant surface and time at a given initial distance. The spectra are given in figures 7 through 14 and summarized in table 3. The 14 mm high grain burns in approximately 60 sec for an average burning velocity of 0.2 mm/s. The average flow calculated is 50 cm/s assuming that the cylindrical geometry is retained throughout the burn (a residual residue retaining approximately the original cylindrical geometry is retained throughout much of the burn). In the middle of the burn, the propellant flame consists of: (1) a dark region extending 4 mm above the propellant surface; (2) a conical dark yellow post flame region above the dark zone and extending to 3 cm above the propellant surface; and (3) a conical blue after-burning diffusion flame of CO , H_2 , and air extending to 8 cm above the propellant surface. The initial region of steepest formation of N_2 occurs from 3 to 6 mm above the propellant surface. The flame was smaller during ignition and extinguishment (the initial and final 10 sec, approximately).

Average spectra (100 scans, 10 sec) were taken as a function of distance from the propellant surface to 6 mm above the surface at intervals of 1 mm. Each spectrum was taken nominally 10 sec after ignition. In addition, time sequences of 10 scans (1 sec) spectra were taken approximately every 6 sec from ignition to extinguishment. For H_2 , the intensity of the signal permitted the acquisition of single-shot spectra.

The N_2 spectrum as a function of distance above the propellant surface is shown in figure 7. N_2 appears at low concentration (<1%) at the propellant surface and gradually increases to final concentration near 6 mm. Time-resolved N_2 spectra at 2 mm above the propellant surface are shown in figure 8. N_2 is seen initially at low concentration and takes more than half the burn time to approach equilibrium concentration.

The CO region is shown in figure 9. CO is seen at higher concentration than N_2 at the surface with an increase in temperature most evident with increasing distance above the surface. A peak at the frequency of HCN at 2086 cm^{-1} was moderately strong at the surface and 1 mm but had decayed by 2 mm to reveal the CO hot band at 2080 cm^{-1} . In addition, N_2 and H_2 S(9) at 2129 cm^{-1} are seen to be in approximately constant ratio to CO above 2 mm. In time-resolved spectra of this region (not shown), near the end of the burn (55 sec after ignition), CO and H_2 are no longer present and only the N_2 resonance is seen.

NO and H_2 S(7) spectra are shown in figure 10 as a function of distance above the propellant surface. NO is seen as a modulation of the non-resonant background. However, since NO has a Raman cross section only half that of N_2 , the concentration of NO may be greater than 1% at the surface. In time-resolved spectra NO is seen to persist until the steep increase in N_2 which occurs at about 4 mm above the propellant surface. The H_2 S(7) band is seen to undergo a continuous increase with distance above the propellant surface up to 6 mm.

Prominent spectra at 1599 cm^{-1} tentatively associated with the RDX NO_2 asymmetric stretch transition reported at 1596 cm^{-1} in the Raman spectrum of RDX powder (Iqbal et al., ref 32), H_2 S(5) at 1446 cm^{-1} , and CO_2 at 1387 cm^{-1} are shown in figure 11. The 1599 cm^{-1} transition is present at the surface and at 1.0 mm but absent at 3.0 mm. The H_2 S(5) transition is seen to increase relative to CO_2 . This is consistent with the final equilibrium concentrations of these species. At 1 mm, the moderate intensity feature between H_2 and CO_2 near 1408 cm^{-1} is seen to be complex and tentatively associable with CO_2 and HCN bending modes (Harris, ref 7).

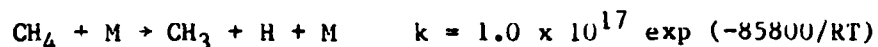
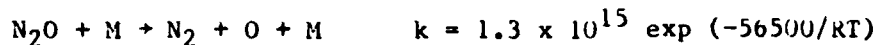
Time-resolved spectra of H_2 Q branch at the propellant surface are given in figures 12 through 14. The H_2 Q branch has a cross section twice as large as nitrogen, and hydrogen is present at high concentration throughout the propellant flame so that the hydrogen Q branch spectra are not perturbed appreciably by the non-resonant susceptibility. This simplified interpretation of the spectra to obtain temperature. As shown in figure 12, single shot spectra are obtained at good signal-to-noise and are in substantial agreement with 10-shot averaged spectra. The reduction of the signal-to-noise from bottom to top is a reflection of the increasing temperature as a function of distance above the propellant surface. Temperatures have been obtained from the H_2 Q branch spectra. The average temperature of the spectra taken at the surface is $1000\text{ K} \pm 200\text{ K}$. The dispersion reflects not only the noise in the individual spectra but also the variation of the distance of the surface with respect to the CARS sampling volume since spectra are taken as close to the surface as possible. A propellant surface/gas interface temperature is more properly associated with the lower bound of the propellant surface temperature measured with good signal-to-noise rather than the average surface temperature. The spectra shown in figure 14 are three-shot averages and are near the lower bound of measured surface/gas interface temperatures. The lower two spectra were least-squares fit to a temperature of $900 \pm 100\text{ K}$ which may then be associated with an upper bound of the surface/gas interface temperature. Time-resolved H_2 Q branch CARS spectra taken at the surface during the duration of the propellant burn were used to obtain temperature. (The spectra used were Boltzmann within experimental accuracy. The non-Boltzmann distributions were not obtained with the frequency encountered in CH_4/N_2O flames.)

These spectra show an initial temperature of 1000 ± 200 K with a gradual rise to 1500 ± 200 K over the first 40 sec of the burn, then a sharp increase within a sec to 2000 ± 200 K which is maintained for approximately 10 sec before a rapid rise to 2600 ± 200 K at 55 sec of the burn. The initial gradual temperature rise to 1500 K may be associated with the dark zone while the steep temperature rise to 2000 K may be associated with the reaction zone of the adiabatic flame which culminates in flame temperature near the calculated adiabatic flame temperature of 2076 K. The subsequent steep temperature rise to 2600 K encountered at 55 sec into the burn is associated with the afterburning or diffusion flame of CO, H₂ with air. This is consistent with the absence of CO and H₂ at this time in time-resolved spectra discussed above. As in the CH₄/N₂O flame, flame stability decreases with distance above the surface of the propellant. Temperature and concentration were also obtained from N₂ spectra in the adiabatic post flame region as 2010 ± 115 K and 0.26 ± 0.04 which are in good agreement with the calculated values (2076 K and 0.22) and the temperature estimated from hydrogen spectra in this region (2000 ± 200 K). (N₂ spectra have not been analyzed in the dark and reaction zones because the composition of these regions is not yet sufficiently characterized to permit estimation of the nonresonant susceptibility.)

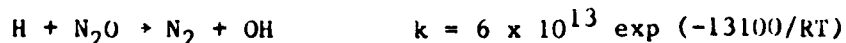
DISCUSSION

The reaction zone of the rich CH₄/N₂O flame was studied primarily to provide a stationary flame analog to the transient nitramine propellant flames. Since the rich CH₄/N₂O flame has similar atomic composition, adiabatic flame temperature, and final products as the propellant flame, it is to be expected that some features of the kinetic mechanisms will be similar in both systems. In the CH₄/N₂O flame, the decay of the initial products was observed through the Q branch of the ν_1 NN and ν_3 NO stretching modes of N₂O and the Q, O, and S branches of the ν_2 and 2 ν_2 modes of CH₄. The formation of the products N₂, H₂, CO, and CO₂ was also observed.

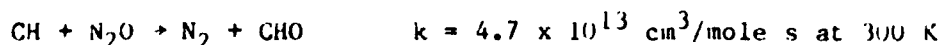
No intermediate species were detected in the spectral range investigated. Initial decomposition of the reactants was observed to occur near 500 K. The first order rate constants for N₂O (Balakhnine et al., ref 33) and CH₄ (Tabayaski and Bauer, ref 34)



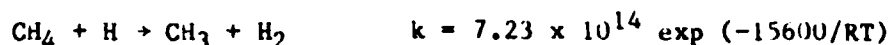
preclude observable reaction at 500 K. However, secondary reactions for N₂O given by Balakhnine



and Wagel et al (ref 35)

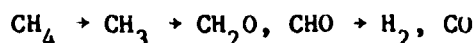


and CH_4 given by Tabayaski and Bauer (ref 34)

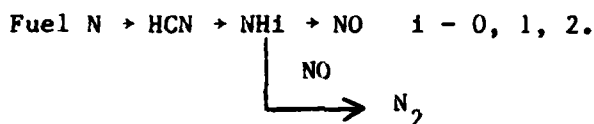


explain reactivity at 500 K.

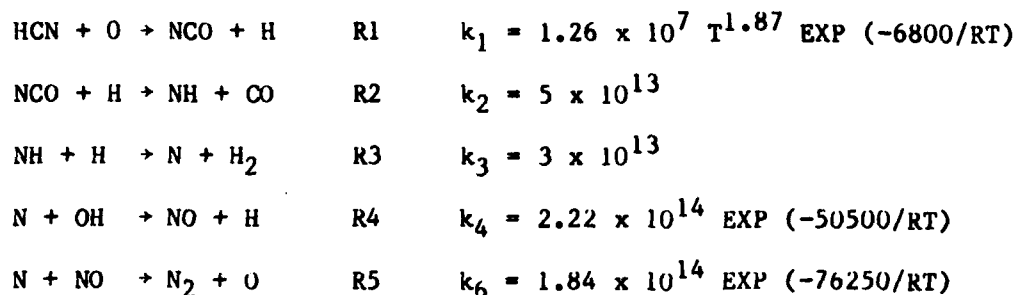
The conversion of methane to final product is thought to proceed by the following global mechanism (Westbrook and Dryer, ref 36)



The conversion of fuel-bound nitrogen is an area of active current research. Recently, $\text{CH}_4/\text{O}_2/\text{AR}$ flames doped with HCN, NO, and NH_3 ; and $\text{H}_2/\text{O}_2/\text{AR}$ flames doped with HCN were studied by Zabielski (ref 37) and Miller et al. (ref 37), respectively. These and previous studies have shown that the conversion of fuel nitrogen to HCN is almost quantitative and independent of the chemical nature of the initial fuel nitrogen. Since conversion to HCN is not rate limiting, research has focused on conversion to NO and N_2 . These processes are thought to occur by the global mechanism.



Good agreement between the theoretical and experimental temperatures and the concentration profiles in these studies has been obtained in terms of the following key reactions:



The reaction constant k_1 is based on a measurement by Perry and Melius (ref 38); k_2 is an estimate (Miller et al., ref 39); and $k_3 - k_5$ are taken from a recent compilation (Miller et al., ref 40). These reactions, with the addition of the hydrocarbon combustion cycle given globally above, account qualitatively for the formation of the principal products H_2 , N_2 , and CO in the rich $\text{CH}_4/\text{N}_2\text{O}$ flame studied here. Further reduction of the data obtained from the $\text{CH}_4/\text{N}_2\text{O}$ flame to quantitative temperature and concentration profiles will enable a quantitative test of these kinetic mechanisms. The results for $\text{CH}_4/\text{N}_2\text{O}$, as presented, provide a comparison for results obtained in nitramine propellants.

In nitramine propellant, the upper bound of the gas-surface interface temperature was measured at 900 ± 100 K. To our knowledge, this is the first direct

measurement of the gas-surface interface temperature in the gas phase. The measured temperature was in good agreement with a propellant surface temperature of 700 K measured in the solid phase using thermocouples (Kubota, ref 12). Near the surface of the propellant reactant, RDX and transient species HCN and NO were observed at moderate concentration (>1%). The final product N_2 was observed at low concentration (~1%) while H_2 and CO were observed at higher concentration (>10%). A gradual temperature rise from the surface to 4 mm above the surface to 1500 K was observed, with a steep rise to 2000 K occurring near 4 mm. RDX and HCN were observed to decay within 2 mm of the surface with NO remaining constant to 4 mm. Near 4 mm, NO decayed rapidly with a concomitant increase in N_2 concentration and temperature to adiabatic flame temperature. H_2 , CO, and CO_2 increased in concentration throughout this region.

The physical structure of the flame is similar to that modeled by Ben-Reuven and Summerfield (ref 11) in terms of near field and far field reactions occurring in the dark zone. However, these results suggest that the chemistry in this model (Ben-Reuven and Caveny, ref 10) must be modified. The observation of HCN and lack of observation of N_2O (<0.1%) is consistent with the high temperature ($T > 600$ K) nitramine decomposition mechanism



NO_2 , although observable at low pressure in CAKS, is not observable at atmospheric pressure--perhaps due to the adsorption by NO_2 in the region of the laser beams used in these experiments. Additional experiments are needed (laser fluorescence is a possibility) to determine the concentration of NO_2 in the reaction zone. NO_2 is presumably converted to NO by fast radical recombination reactions of NO_2 with H, N, and O (Baulch et al., ref 41).

Thus RDX decomposition in the flame differs from processes occurring in the CH_4/N_2O flame in that RDX decomposes directly into products that are thought to be the principal intermediates in the conversion of fuel-bound nitrogen to final products. This allows, in contrast to CH_4/N_2O processes, a substantial buildup of the intermediates HCN and NO near the propellant surface so that they are directly observable in CAKS.

At these pressures, it is the decomposition processes of the species at the surface, RDX and HCN, which supply the heat that determines the burning rate of the nitramine propellant. NO conversion to N_2 which provides the heat for the luminous flame occurs too far upstream to affect the surface. HCN decomposition processes, which are given above, are initiated by R1. Since R1 depends on the oxygen concentration, the ignition of nitramine propellants depends critically on oxygen concentration. The steep rise in temperature to 2600 K indicates the presence of the afterburning reaction of hot CO and H_2 (which constitutes 65% of the products) with air. This reaction serves to shield the inner flame from the influence of atmospheric oxygen and serves as a flame holder for the inner flame.

CONCLUSIONS

The reaction zone of nitramine propellant is seen to consist of two characteristic areas: (1) an inner flame area near the solid gas-interface which is at a temperature of 900 ± 100 K and is characterized by the gas-phase reactions of RDX and HCN that provide the heat that determines the burning rate, and (2) an outer flame area farther upstream where NO is converted to N_2 to generate the luminous flame.

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Table 1. Laser dyes

Dye	Solvent	Concentration ($\times 10^5$ M)		Nonresonant background		Species observed
		Oscillator	Amplifier	I_{\max} (cm^{-1})	FWHM (cm^{-1})	
DCM	EtOH	5.8	0.6	4210	300	$\text{H}_2(\text{Q})$
LDS698		2.0	2.0			
DCM	EtOH	25	8.4	3930	420	$\text{H}_2(\text{Q})$
LDS698		16	5.4			H_2O
Rh640	MeOH	44.5	4.1	3920	150	$\text{H}_2(\text{Q})$
Ox725	(NaOH)	7.8	1.5	2270	110	N_2
LD690	MeOH	25	8.3	3390	80	CH_4 overtones
				3225	70	
LD690	MeOH	15	8.3	3190	95	CH_4 overtones
Rh640	MeOH	24	3.2	2300	110	$\text{N}_2, \text{N}_2\text{O}$
Kiton red	MeOH	10	10	2180	150	$\text{N}_2\text{O}, \text{CO}, \text{HCN},$
Rh640		3	3			$\text{H}_2(\text{S})$
Kiton red	MeOH	21	2.8	1860	100	$\text{NO}, \text{H}_2(\text{S})$
Rh640		4.5	0.3			
Kiton red	MeOH	21	2.8	1820	110	$\text{NO}, \text{H}_2(\text{S}), \text{O}_2$
Rh640		2.8	0			
Kiton red	MeOH	23	2.8	1730	110	$\text{H}_2(\text{S}), \text{O}_2,$
						$\text{CH}_4(\text{S})$
Kiton red	EtOH	23	2.8	1660		$\text{O}_2, \text{CH}_4(\text{S})$
Rh610	MeOH with 4 drops saturated NaOH	21	3.7	1540	110	$\text{CH}_4, \text{H}_2(\text{S}),$
						CO_2, O_2
	EtOH with aqueous NaOH			1335	100	$\text{CO}_2, \text{H}_2(\text{S}),$
						N_2O

Table 2. Summary of species identified in a $\phi = 3.2$ $\text{CH}_4/\text{N}_2\text{O}$ flame

<u>Observed I_{max} (cm^{-1})</u>	<u>Species</u>	<u>Comment</u>
4155-4075	H_2 Q-branch	Temperature calculations indicate a temperature of 500 K in preheat zone.
3240-3100	CH_4 ($2 \nu_2$)	Rapid decrease in reaction zone
2325	N_2	Gradual increase in reaction zone
2222	N_2O (ν_3)	Rapid decrease in reaction zone
2136	CO	Increase in reaction zone
2129	H_2 S(9)	Rapid increase of intensity in reaction zone; large compared to CO
1813	H_2 S(7)	Signal intensity increases up the reaction zone
1636	H_2 S(6)	Weak signal seen in post flame
1531	CH_4 (ν_2)	Gradual decrease in reaction zone
1447	H_2 S(5)	Signal intensity increases up the reaction zone
1294	N_2O (ν_1)	Intense signal that decreases rapidly in reaction zone

Table 3. Summary of species identified in nitramine propellant flame

<u>Observed I_{\max} (cm^{-1})</u>	<u>Species</u>	<u>Comment</u>
4155-4075	H ₂ Q - branch	Temperature calculations indicate a temperature of 900 K at the surface of the propellant
2325	N ₂	Slow increase until near the end of reaction zone, a large increase occurs
2136	CO	Signal increases up reaction zone
2129	H ₂ S(9)	Observed similar intensity to CO
2086	HCN (ν_1)*	Strong signal initially which diminishes rapidly
1872	NO	Low concentration modulation which remains constant throughout reaction zone; decreases rapidly at end of reaction zone
1814	H ₂ S(7)	Signal intensity increases up the reaction zone
1599	RDX (NO ₂ asymmetric stretch)*	Moderate concentration early in the reaction zone
1447	H ₂ S(5)	Signal intensity increases up the reaction zone
1387	CO ₂ (ν_1)	Moderate signal early in reaction

* Tentative.

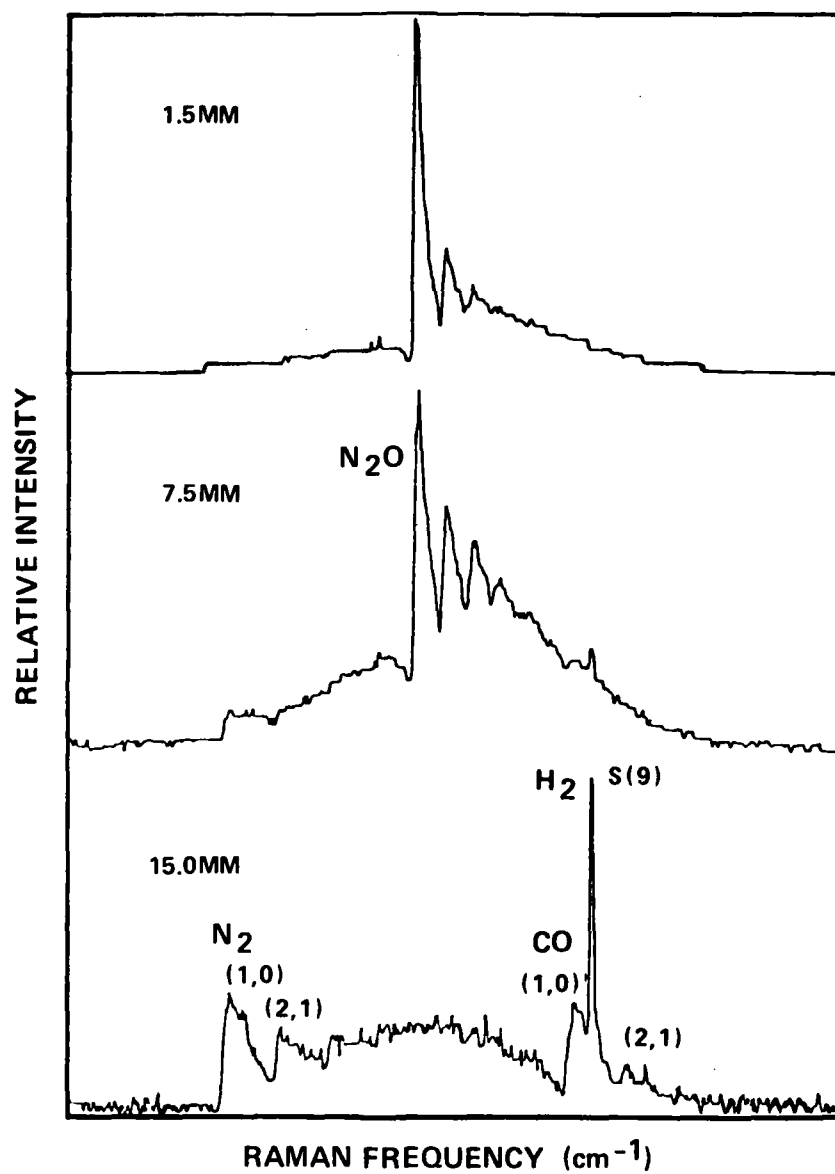


Figure 1. CARS spectra of N_2O , CO , N_2 , and H_2 S(9) from a $\phi = 3.2$ $\text{CH}_4/\text{N}_2\text{O}$ flame

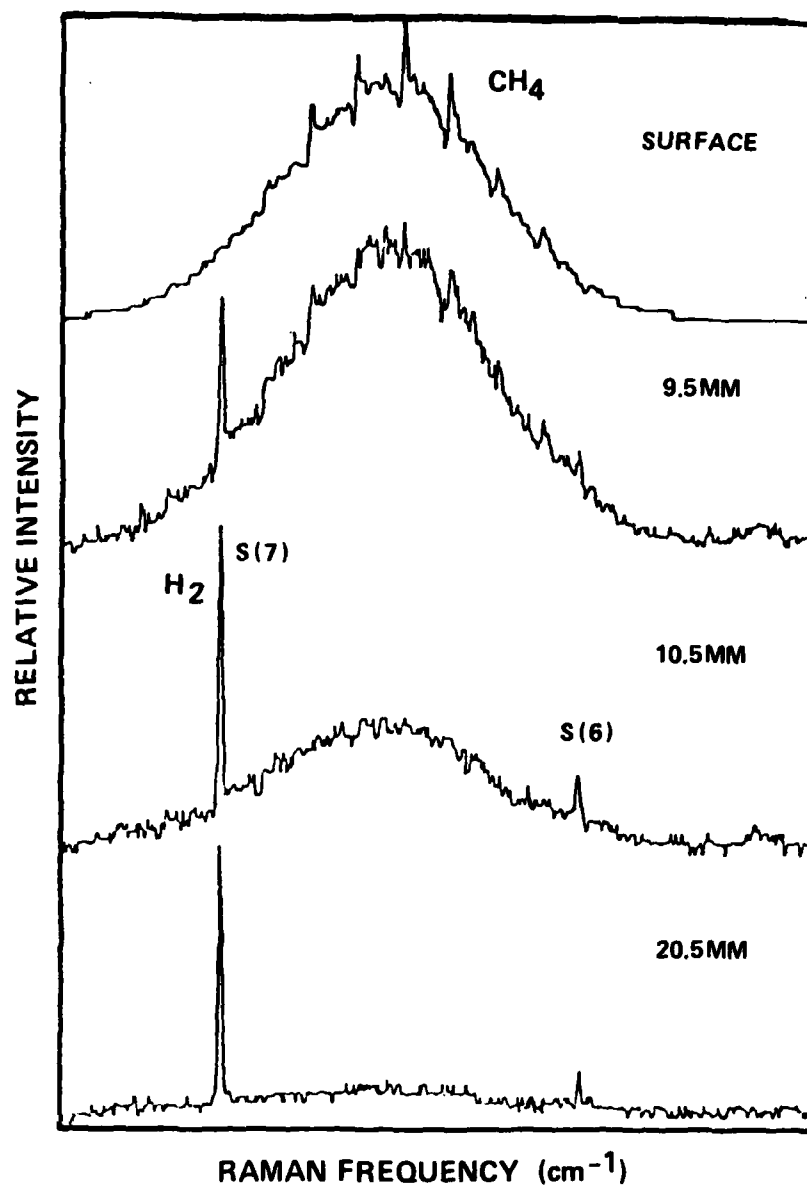


Figure 2a. CARS spectra of CH₄ (ν_2) and H₂ S(7) and S(6) from a ϕ 3.2 CH₄/N₂O flame

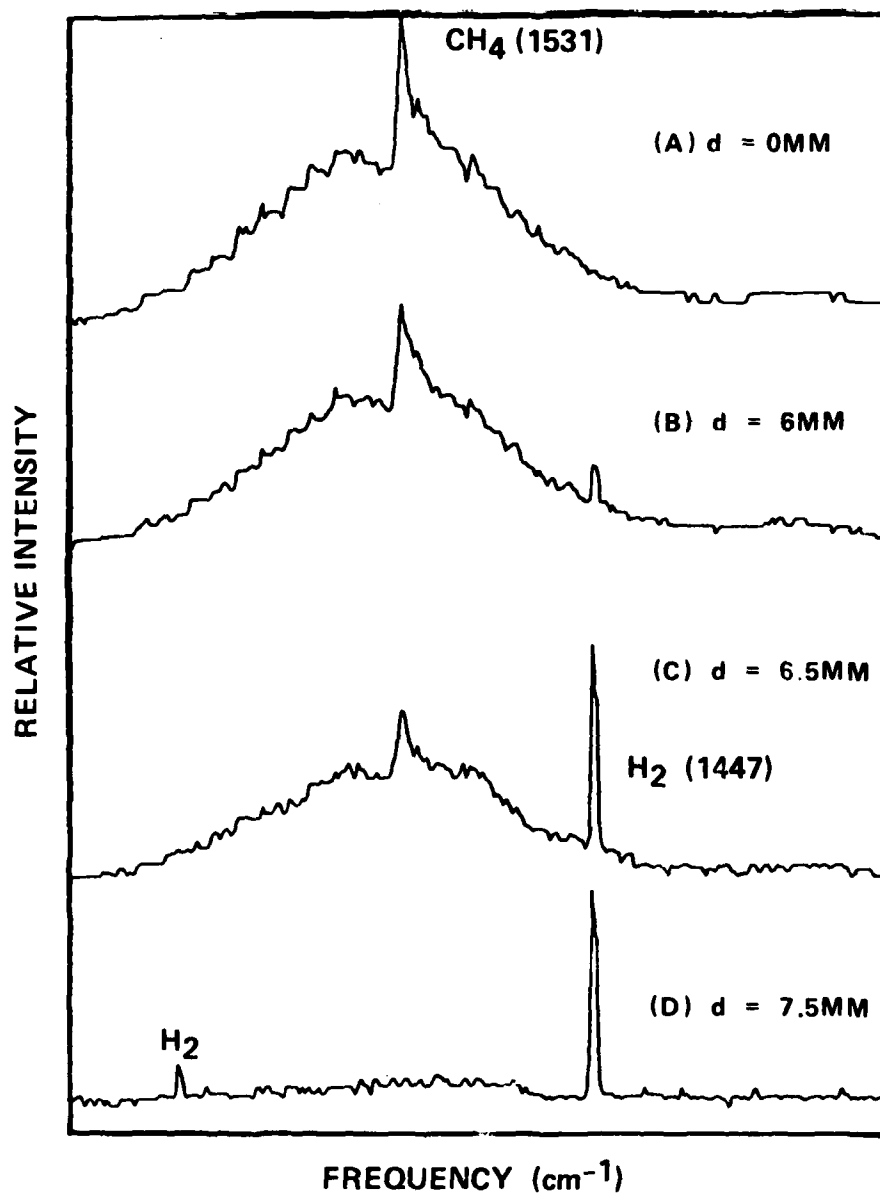


Figure 2b. CARS spectra of CH₄ (ν_2) and H₂ S(5) and S(6) from a $\phi = 3.2$ CH₄/N₂O flame

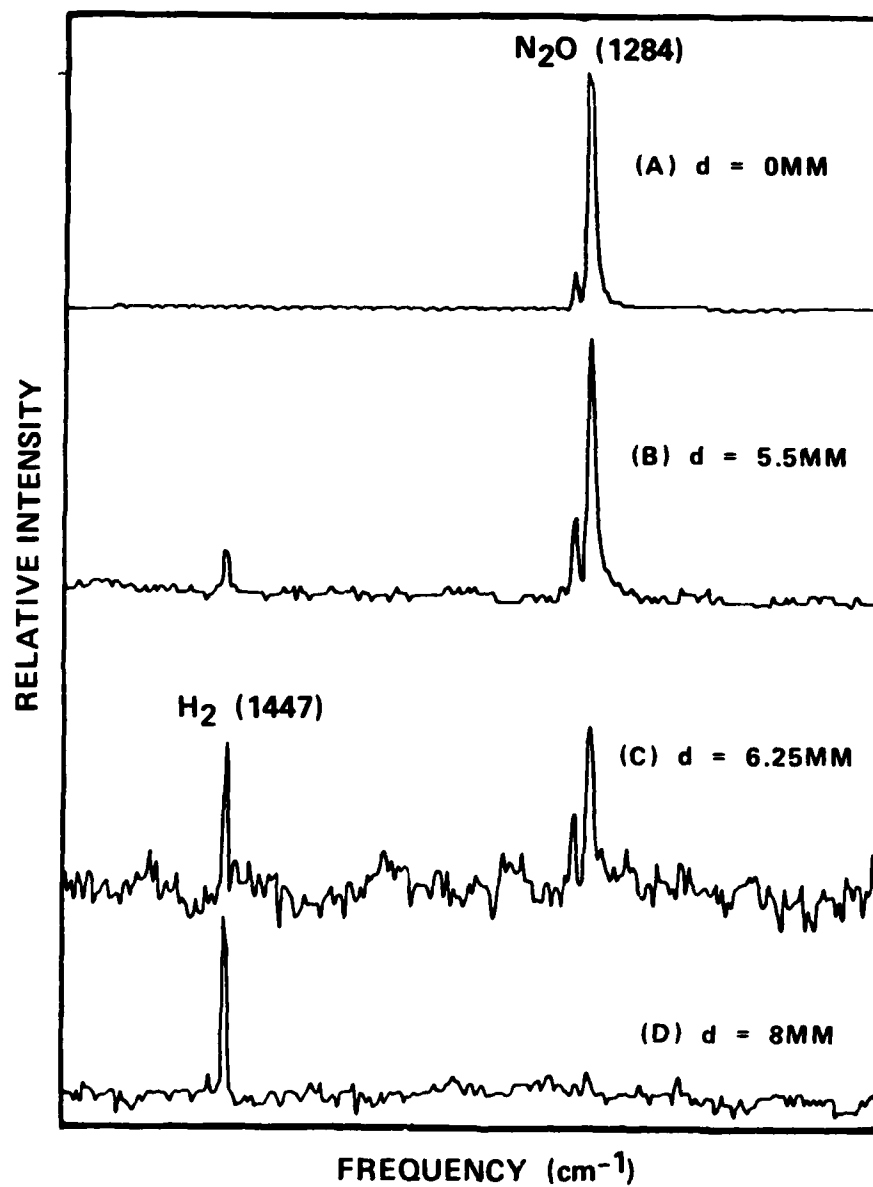


Figure 3. CARS spectra of N₂O and H₂ S(5) from a $\phi = 3.2$ CH₄/N₂O flame

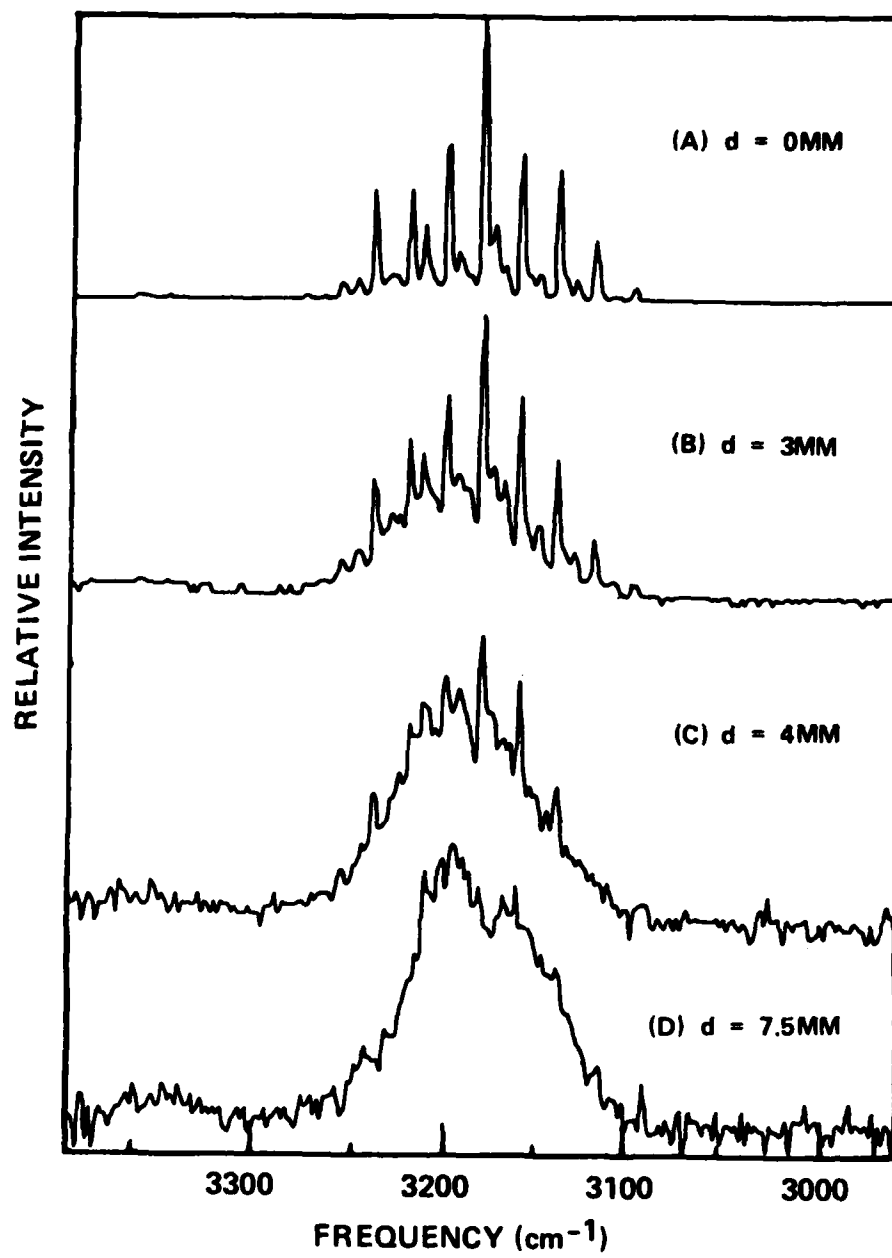


Figure 4. CARS spectra of CH_4 ($2\nu_2$) from a $\phi = 3.2$ $\text{CH}_4/\text{N}_2\text{O}$ flame

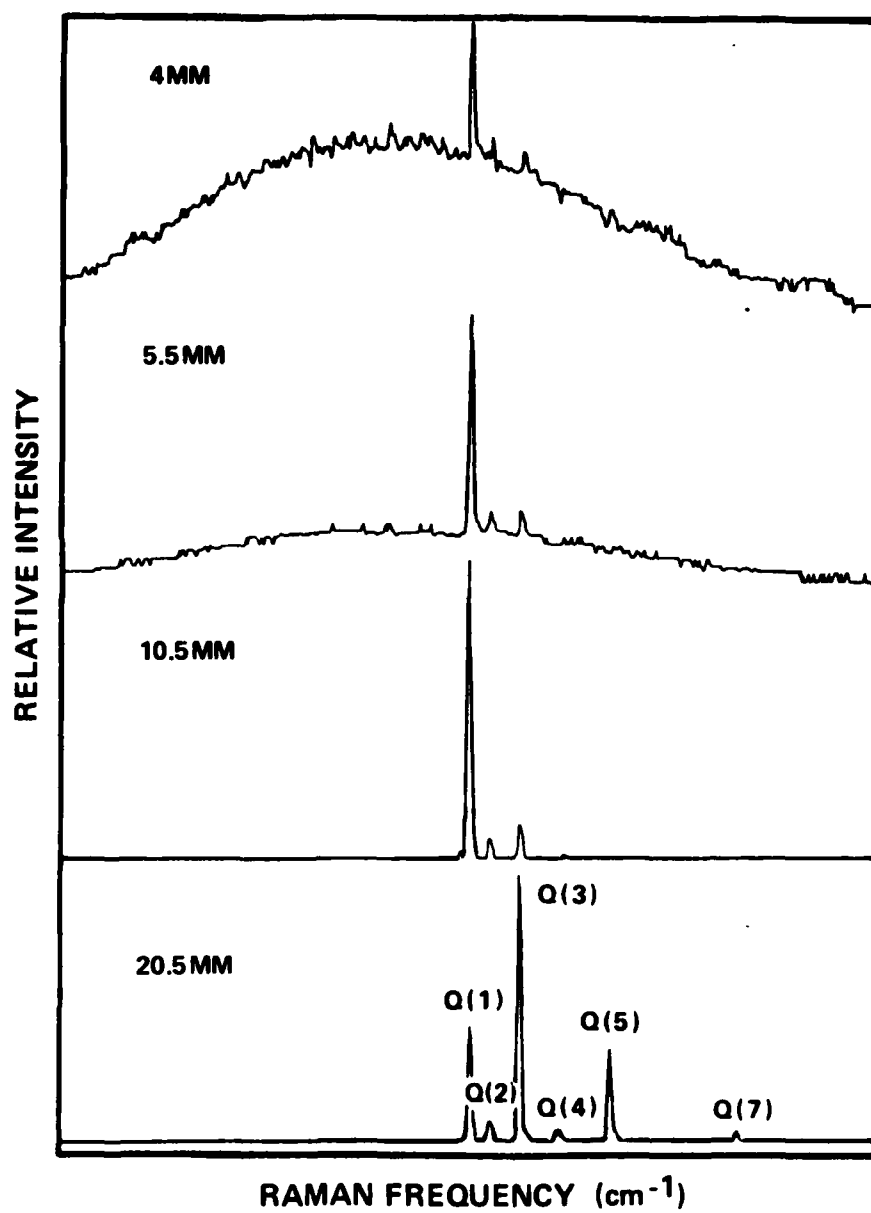


Figure 5. CARS spectra of H₂ Q-branch ($v'' = 0$) in a $\phi = 3.2$ CH₄/N₂O flame

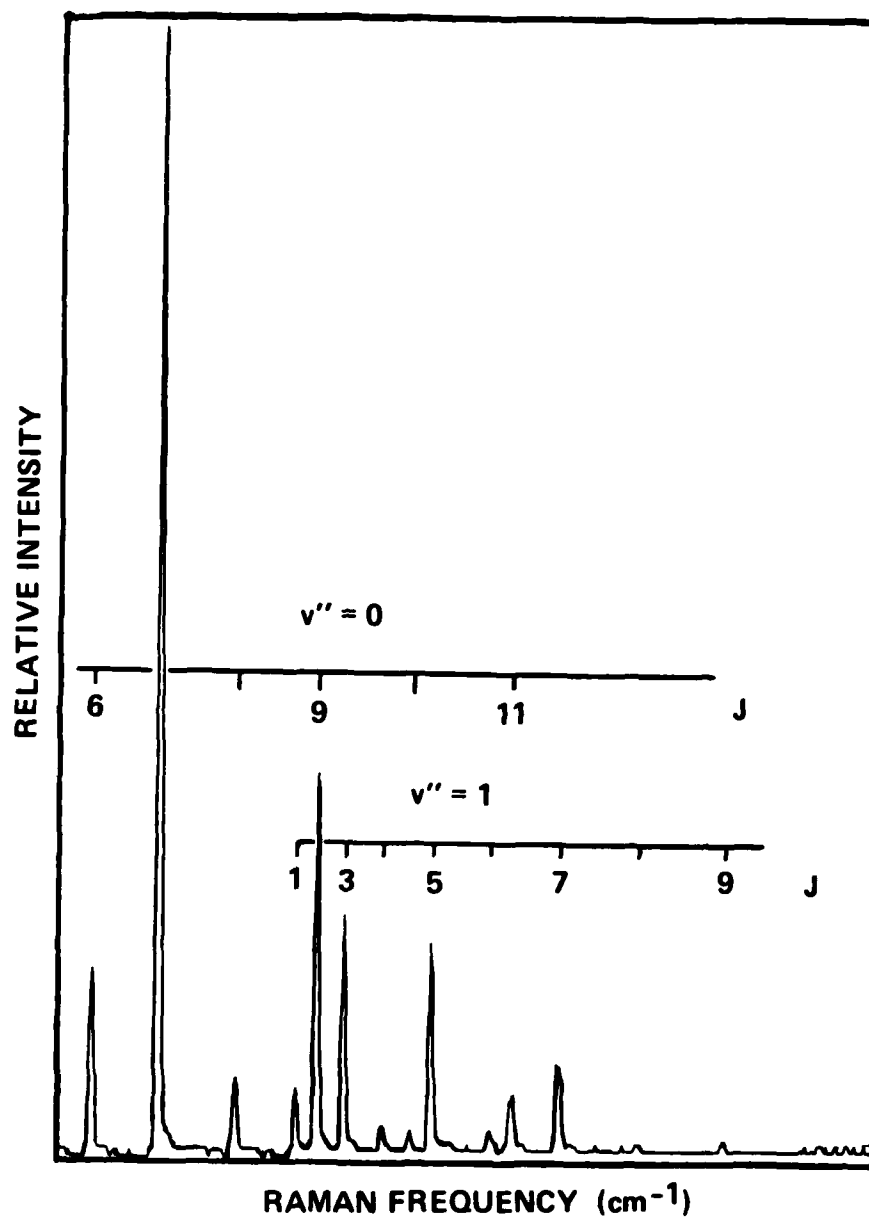


Figure 6. CARS spectra of H₂ Q-branch ($v'' = 0$ and $v'' = 1$) in a $\phi = 1.8$ CH₄/N₂O flame

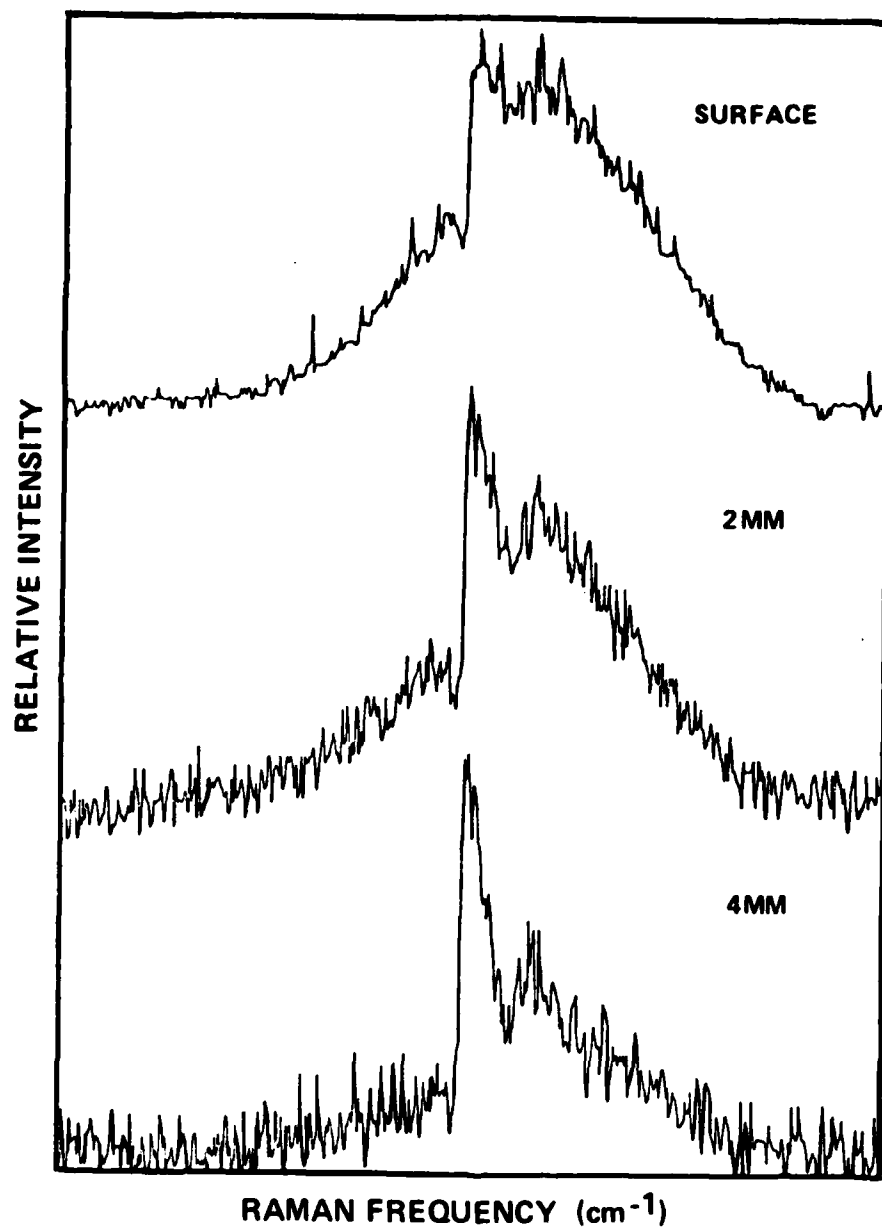


Figure 7. Time-averaged CARS spectra of N_2 at various distances above the surface of a nitramine propellant flame

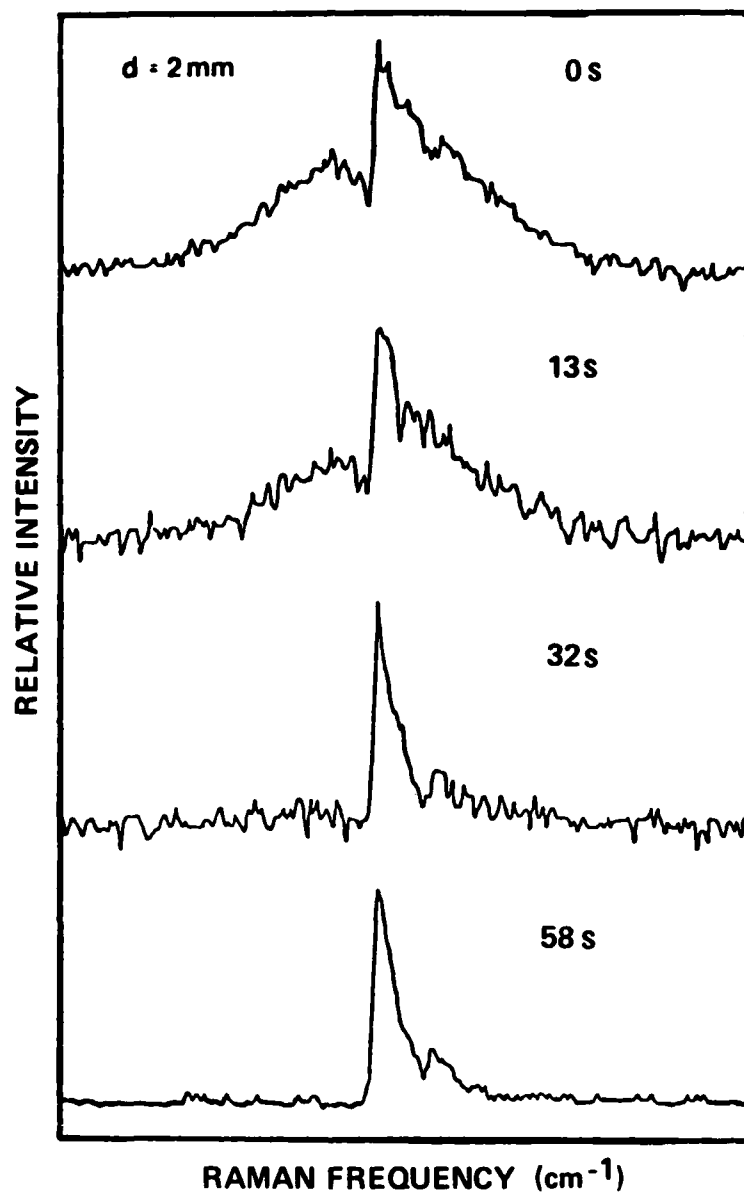


Figure 8. Time-resolved CARS spectra of N_2 at various times after ignition at 2-mm above the surface of a nitramine propellant

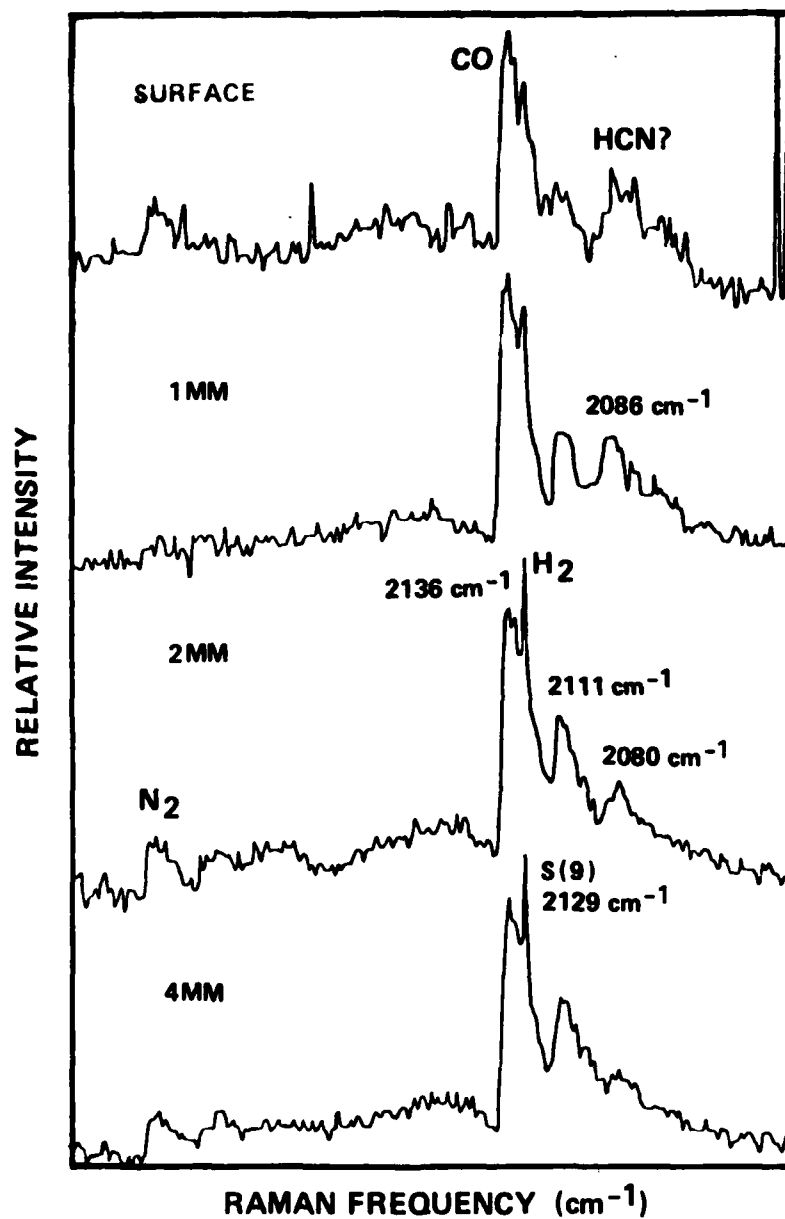
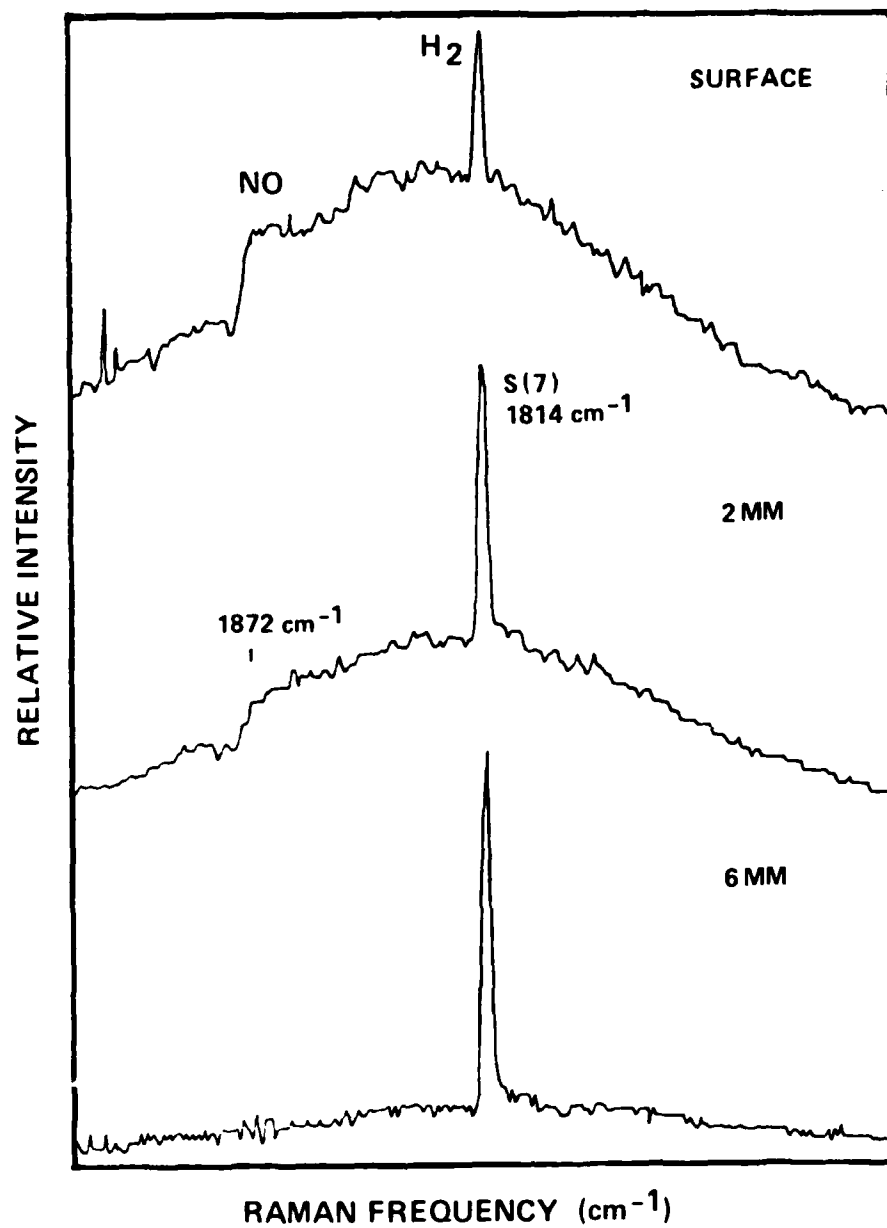
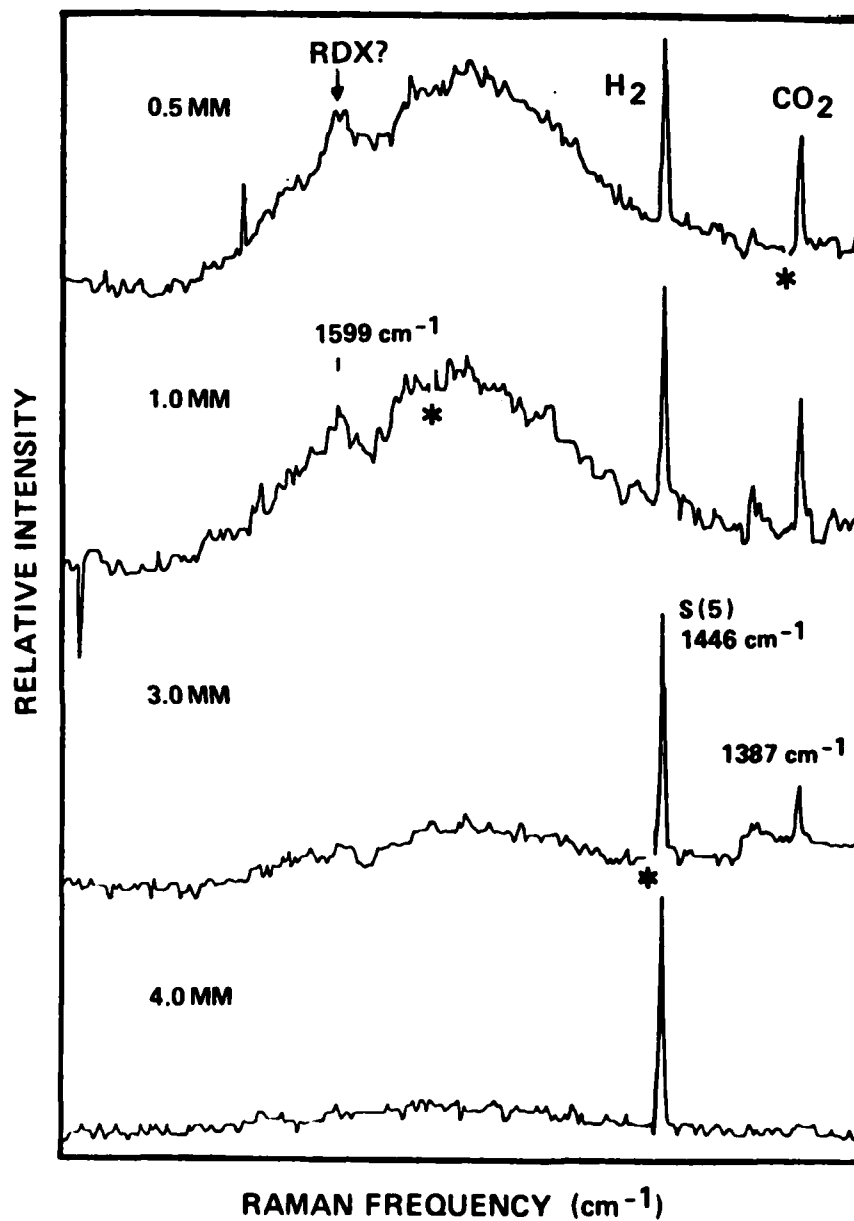


Figure 9. Time-averaged CARS spectra of HCN, CO, N₂, and H₂ S(9) above the surface of a nitramine propellant flame



10. Time-averaged CARS spectra of NO and H_2 S(7) above the surface of a nitramine propellant



* FOR CLARITY, SPIKES
DUE TO ARCING NEAR
THE PROPELLANT SUR-
FACE HAVE BEEN RE-
MOVED.

Figure 11. Time-averaged CARS spectra of RDX (tentative), H₂ S(5), and CO₂ above the surface of a nitramine propellant

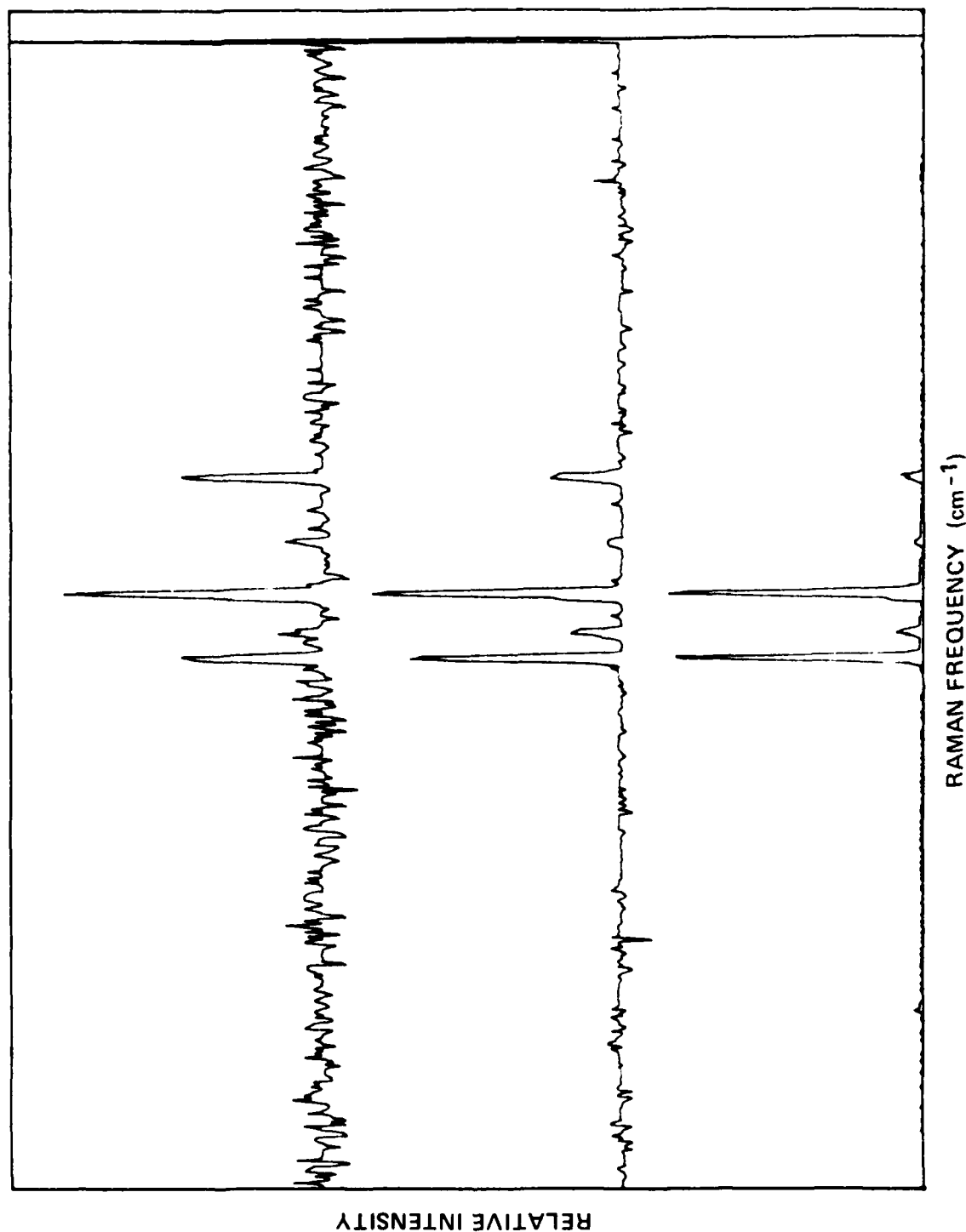


Figure 12. Time-resolved (single shot) CARS spectra of the H₂ Q branch taken at nominal 6-second intervals after ignition, and shown sequentially from bottom to top

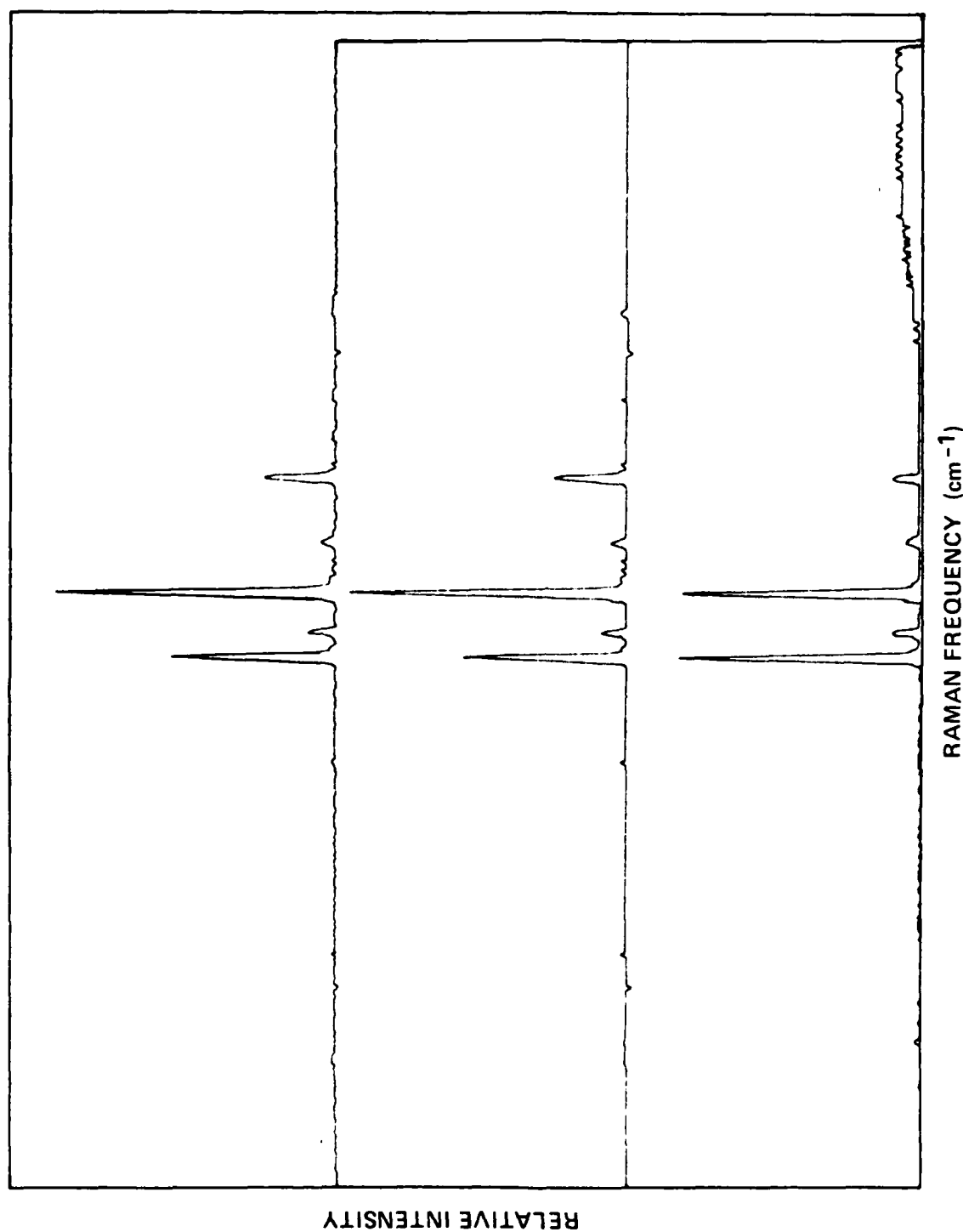


Figure 13. Time-resolved (10-shot averaged) CARS spectra of the H_2 Q branch taken at nominal 6-second intervals after ignition and shown sequentially from bottom to top

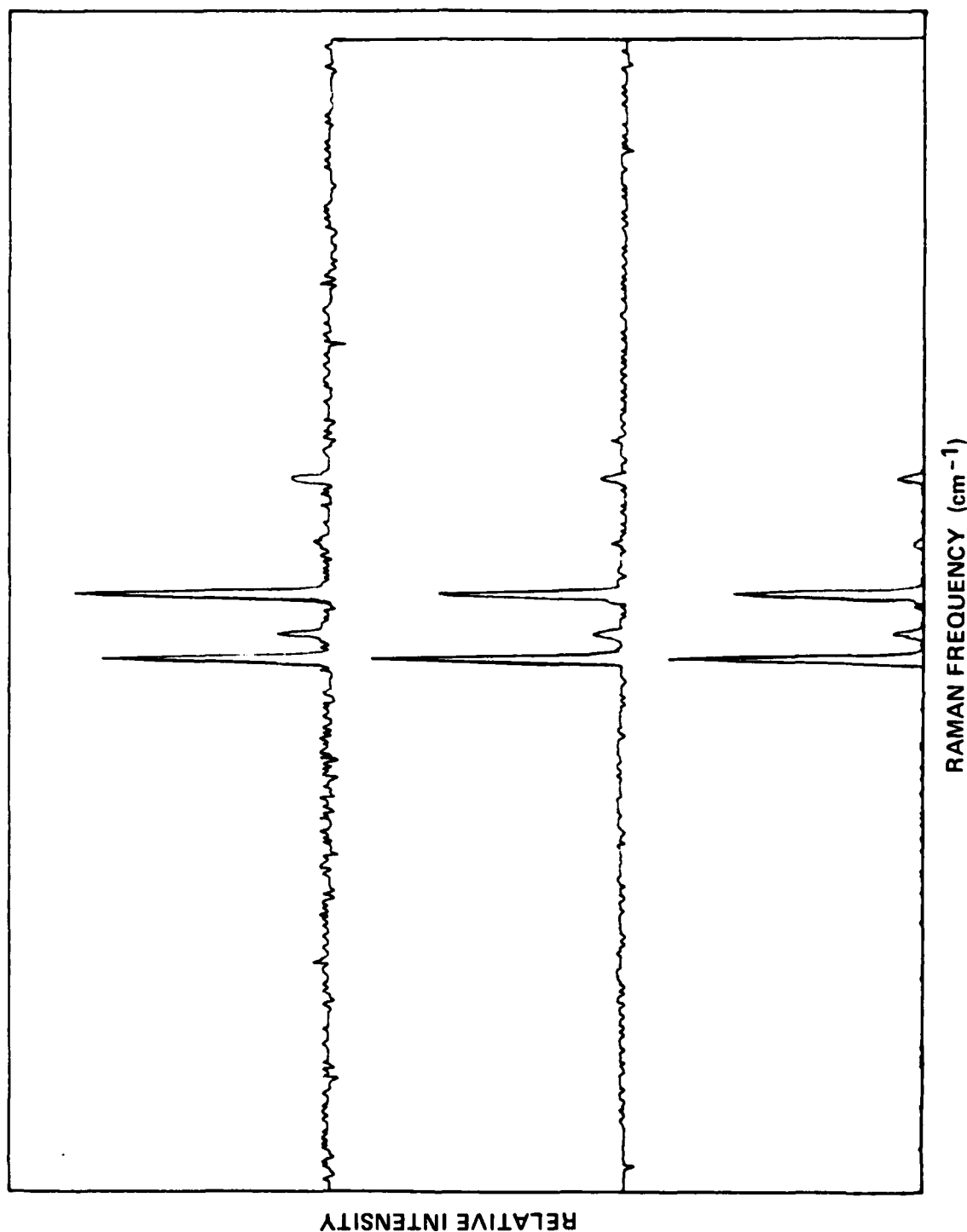


Figure 14. Time-resolved (3-shot averaged) CARS spectra of the H_2 Q branch taken at nominal 6-second intervals after ignition and shown sequentially from bottom to top

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